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SUMMARY

Sulfur in fuels can be accurately measured using an ion chromatograph and a modified Parr bomb oxidation. The fuel samples were burned in a Parr oxygen bomb that was purged four times with oxygen and contained 20 ml of 0.003 M sodium bicarbonate (NaHCO_3) + 0.0024 M sodium carbonate (Na_2CO_3) eluent. The resulting sulfate was measured using an ion chromatograph and then the sulfur content was calculated. Analysis of Standard Reference Materials, from the National Bureau of Standards, of $\sim 0.2 \pm 0.004\%$ sulfur, produced results with a standard deviation no greater than 0.008. The ion chromatographic method can also be applied to conventional fuels and shale-oil derived fuels. Other acid forming elements, such as fluorine, chlorine and nitrogen could also be determined at the same time, provided these elements have reached a suitable ionic state during the oxidation of the fuel.

INTRODUCTION

The national energy crisis prompted NASA Lewis Research Center to investigate the possibility of using alternate fuels in jet aircraft, turbine engines and in other areas. The properties of these alternate fuels are being studied to insure that they will perform in the same manner as the more conventional fuels. One property under investigation is the sulfur content. Control of the sulfur content is important for fuels that are to be burned in engines. The sulfur oxides formed during combustion may combine to form corrosive acids that can corrode engine parts. Or, the oxides may contribute to air pollution problems.

A review of the literature disclosed the following methods for the determination of sulfur in fuels. The fuel can be oxidized, usually in a Parr oxygen bomb, and the resulting sulfate can be titrated with sodium hydroxide (ref. 1) potassium iodate (ref. 2), or barium chloride (ref. 4). Or, sulfate can be precipitated and weighed as barium sulfate (refs. 3, 5, and 6).

The method discussed in this paper uses ion chromatography to determine the sulfate produced by a modified Parr bomb oxidation of the fuel. Standard Reference Materials (SRM's) of approximately 0.2% sulfur, supplied by the National Bureau of Standards, were used to verify the precision and accuracy of the method. SRM's with lower sulfur concentrations were not available for evaluation. Never the less, other fuel samples, with lower sulfur concentrations were also analyzed. These included Jet-A fuel and two jet fuels derived from shale-oil prepared by the TOSCO procedure. The results from these analyses, however, cannot be compared to any standard materials.

There are several advantages in using the ion chromatographic method instead of the other referenced methods. First, the only reagents needed are sodium bicarbonate and sodium carbonate to make up the eluent. Second, an analysis, including oxidation of the fuel, can be completed in 45 minutes. Third, substances, such as iron, that may interfere with other methods (ref. 3) do not interfere with the ion chromatographic method. Nitrogen is the only substance that has caused any interference with the method. This interference and techniques to reduce it will be discussed. Finally, other anions formed during oxidation of the fuel can also be detected, such as chloride, fluoride, nitrite and nitrate.

APPARATUS

The test equipment used are the following:

1. Dionex Model 10 Ion Chromatograph - The parameters used for this instrument were those recommended by Dionex for general anion analysis. Three anion separator columns were used. First, a 3×150 mm pre-column, second, a 3×500 mm separator column, both filled with a low capacity anion exchange resin. Third, a 6×250 mm suppressor column filled with a high capacity cation exchange resin. A sampling loop of 100 μ l was used with a pumping speed of 110 ml per hour.

2. Parr 1341 Plain Jacket Oxygen Bomb Calorimeter - A stainless steel combustion capsule, 2.54 cm in diameter and 1.11 cm deep, was used to hold the sample. The sample was ignited using a nickel-chrome wire and a 2901 ignition unit.

3. 5 ml Syringe - The syringe was equipped with a 7.62 cm blunt end needle, with a standard female luer and a 13 mm in diameter stainless steel filter holder containing a glass fiber filter. The filter was capable of removing particles greater than 0.3 μ with 99.97% efficiency.

Reagents (Materials)

The following reagents and materials were used:

1. Reagent Grade Sodium Bicarbonate (NaHCO_3)
2. Reagent Grade Sodium Carbonate (Na_2CO_3)
3. Reagent Grade Potassium Sulfate
4. Reagent Grade Potassium Nitrate
5. Benzoic Acid
6. Deionized water, with a specific resistance greater than 1 megohm.
7. Eluent, a mixture of 0.003 M NaHCO_3 + 0.0024 M Na_2CO_3
8. Oxygen, conforming to MIL-0-2721 OD(ASG) specifications for at least 99.5% purity.
9. National Bureau of Standards, SRM's - 1623 Residual Fuel, 0.268% sulfur; 1624 Distillate Fuel, $0.211 \pm 0.004\%$ sulfur
10. Jet-A Fuel
11. #33366 TOSCO shale-oil
12. #33368 TOSCO shale-oil

PROCEDURE

A fuel sample of ~0.8000 g was weighed into the combustion capsule and placed into the Parr oxygen bomb which contained 20 ml of accurately measured chromatographic eluent. The bomb was purged four times with oxygen to a pressure of 4 atmospheres and then depressurized. After purging, oxygen was added to the bomb to a pressure of 25 atmospheres. The bomb was immersed in the calorimeter and the sample was ignited and allowed to burn for ~10 minutes. After combustion, the bomb was depressurized and 80 ml more of eluent were accurately added. The bomb was sealed and the sample-eluent solution was thoroughly mixed, by shaking, for 1 minute. After mixing, a 1 milliliter sample was taken from the bomb, using the filter syringe, and injected into the ion chromatograph for analysis which produced a chromatogram typical of that shown in figure 1.

The sulfate peak, of the SRM's, was measured with no difficulty, and the sulfur content was calculated. The resulting sulfate peak, of the low sulfur fuels, was determined by using an overlay chromatogram to find the true sulfate baseline. Nitrate concentrations in excess of 3 to 4 times that of the sulfate peak can cause an interference to the determination of sulfate. Excessive nitrate (with an elution time of

9.9 min) will cause a "bleeding" of the nitrate peak into the sulfate peak which elutes at 14 minutes. The sulfate will appear as a shoulder on the nitrate peak. The overlay chromatogram was produced by using a standard nitrate solution of the same concentration as that found in the fuel. By superimposing the overlay chromatogram on the chromatogram produced by the fuel, a true sulfate baseline was traced in. Once the true baseline was established for the sulfate peak, the concentration of the sulfur was determined. This overlay chromatogram is shown in figure 1.

Calculations

1. Sulfate Content

$$C_{SO_4} = \frac{CH_{SO_4}}{H}$$

C_{SO_4} = The concentration of sulfate in the fuel in ppm

C = The concentration of a standard sulfate solution in ppm

H_{SO_4} = The sulfate peak height of the fuel in divisions

H = The standard sulfate peak height in divisions

2. Sulfur Content

$$\text{Percent Sulfur} = \frac{C_{SO_4} \times D \times F \times 10^{-6} \times 100}{W}$$

D = A dilution factor, in this case, 100

F = A conversion factor for sulfate to sulfur, 0.333

W = Weight of the sample in grams.

RESULTS AND DISCUSSION

The results of a series of analyses of the two SRM's are shown in table 1. The data is the result of oxidizing each fuel five individual times and analyzing the oxidation products three times each. The maximum difference in 30 analyses was 0.027. This compares favorably with ASTM procedure D129-64. "Test for Sulfur in Petroleum Products by Bomb Method" (ref. 5), which has a repeatability of 0.04. The average sulfur content of National Bureau of Standards (NBS) SRM 1623 Residual

fuel was 0.271% sulfur with a standard deviation of 0.0077%, the reported NBS value was 0.268% sulfur. The average sulfur content of NBS, SRM 1624 Distillate Fuel was $0.214 \pm 0.006\%$ sulfur. The reported NBS value was $0.211 \pm 0.004\%$ sulfur.

Analyses of several Jet-A fuels indicated that a concentration as low as 2 ppm sulfate could be detected. Similar results were obtained using the barium chloride precipitation method. The 2 ppm detection limit is comparable to ASTM procedure D2785-70, "Test for Trace Quantities of Total Sulfur (Wickbold Beckman Combustion Apparatus)" (ref. 7), which has a detection limit of 2 ppm sulfate.

Figure 2 shows a chromatogram from 0.8343 g of TOSCO Shale Oil #33366. The chromatogram was produced using a more sensitive attenuation setting for sulfate than above. The sulfate peak is just detectable as a shoulder of the nitrate peak. Using an overlay chromatogram, 0.2 ppm sulfate was estimated. This would indicate that the ion chromatographic method has a potential detection limit less than the turbidimetric method (ref. 8), which has a lower limit of 1 ppm sulfate.

The ion chromatographic method, like many other methods (refs. 4 to 6), uses the Parr oxygen bomb to oxidize the available sulfur in fuels to sulfate. Two modifications were made on the Parr oxidation procedure to make it applicable to the ion chromatographic method. The first modification involves adding 20 ml of chromatographic eluent to the bomb instead of 1 ml of water, as suggested in the Parr Manual (ref. 6). The eluent effectively absorbs the mineral acids formed during combustion and eliminates the need to wash the bomb to remove the sulfate before analysis. The second modification is a purging process which does not appear to be a part of any other method that uses the oxygen bomb. These methods include ASTM procedure D129-64, the Parr Method and work done by Siegfriedt, Wiberley and Moore (refs. 4 to 6). None of these require purging the bomb. These methods are adequate if nitrate does not interfere with the sulfate analysis. Nitrate interferes with the ion chromatographic analysis of sulfate when it is in concentrations three or more times that of the sulfate. When this occurs the elution time of the nitrate peak, 9.9 minutes, spreads into the sulfate elution time of 14.0 minutes. The sulfate peak then appears as a shoulder on the nitrate peak. This causes the sulfate baseline to shift and necessitates the use of the overlay to accurately measure the sulfate peak height. The nitrate could be formed by the combustion of the fuel or by the oxidation of nitrogen trapped in the bomb when it is sealed. The Parr procedure, for gross heat of combustion (ref. 6), requires corrections for nitrate formed by this trapped nitrogen.

A purging process to remove trapped nitrogen was investigated using Benzoic Acid as the sample. In the first test, the bomb was pressurized to 25 atmospheres of oxygen, without purging. The chromatogram in figure 3 shows that an attenuation

setting of 100 μ MHO was needed to keep the nitrate peak on scale. A second test was conducted in which the bomb was purged four times with 4 atm of oxygen and pressurized to 25 atm. The chromatogram of figure 4 shows that the nitrate peak stayed on scale with an attenuation setting of only 10 μ MHO. Purging produced a ten fold decrease in the nitrate concentration. A third test was conducted in which the bomb was purged eight times before pressurization. The chromatogram of figure 5 indicates that no further significant decrease in the nitrate concentration was achieved by the four additional purgings. The nitrate that remained after the purgings was most probably due to nitrogen that is present in the oxygen. Mass spectrometric analysis of the bottled oxygen indicated that it contained 0.4068% by volume nitrogen. Oxidation of only a small portion of this nitrogen, at 25 atmospheres, could produce all of the nitrate found in either of the last two tests.

The ion chromatograph is also capable of detecting many anions formed during the oxidation of the fuel. Table 2 lists the elution times of the anions that were found in the fuels analyzed. The detection of other anions speeds fuel analyses. Currently, separate analyses are generally performed if other acid-forming elements are determined in a fuel. With the ion chromatographic method these analyses can be completed using the data from one chromatogram. For example, figure 6 shows a chromatogram from TOSCO #33368 shale oil. The fuel was analyzed to determine its sulfur content, but none was found. However, determinations of other observed acid forming elements could be made.

CONCLUSION

To summarize, Parr bomb oxidation combined with the ion chromatograph is a rapid, sensitive and accurate way to determine the sulfur content of fuels. This method can also lend itself to the analysis of other acid-forming elements in these fuels. Large concentrations of nitrogen appear to be the only substance that interferes with this method. Purging techniques suggested in this procedure should eliminate the interference caused by nitrogen trapped in the bomb. However, it will not eliminate nitrates or nitrogen found in the fuels. It is hoped that a technique can be developed to reduce nitrate interference. This might be accomplished by removing nitrate from the sample solution. That is, by treating the sample solution with Devarda's Metal (ref. 8) or Nitron (ref. 9). Satisfactory results might also be obtained by changing the parameters of the ion chromatograph. Use of a weaker eluent, a lower flow rate, a longer separator column or any combination of these should result in a greater separation of the eluted species.

If the nitrate and sulfate peaks can be separated by an additional 2 or 3 minutes, there would no longer be any significant interference from nitrates. This might improve the sensitivity of the ion chromatographic method even further. It may even be possible to detect sulfur in some alternate fuels that at this time show no evidence of its presence. *

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* Mention of a specific company or product does not constitute endorsement by the National Aeronautics and Space Administration.

TABLE 1. - RESULTS OF ANALYSES OF NBS

STANDARD REFERENCE MATERIALS #1623,

0.268% S, AND #1624, 0.211% S

Sample	Max % sulfur	Min. % sulfur	Avg % sulfur	Maximum difference	Standard deviation
1623	0.290	0.263	0.271	0.027	0.0077
1624	.221	.196	.214	.025	.006

TABLE 2. - TABLE OF

ELUTION TIMES

Anions	Time, min
Fluoride (F^-)	2.7
Chloride (Cl^-)	4.0
Nitrite (NO_2^-)	5.0
Nitrate (NO_3^-)	9.9
Sulfate (SO_4^-)	14.0

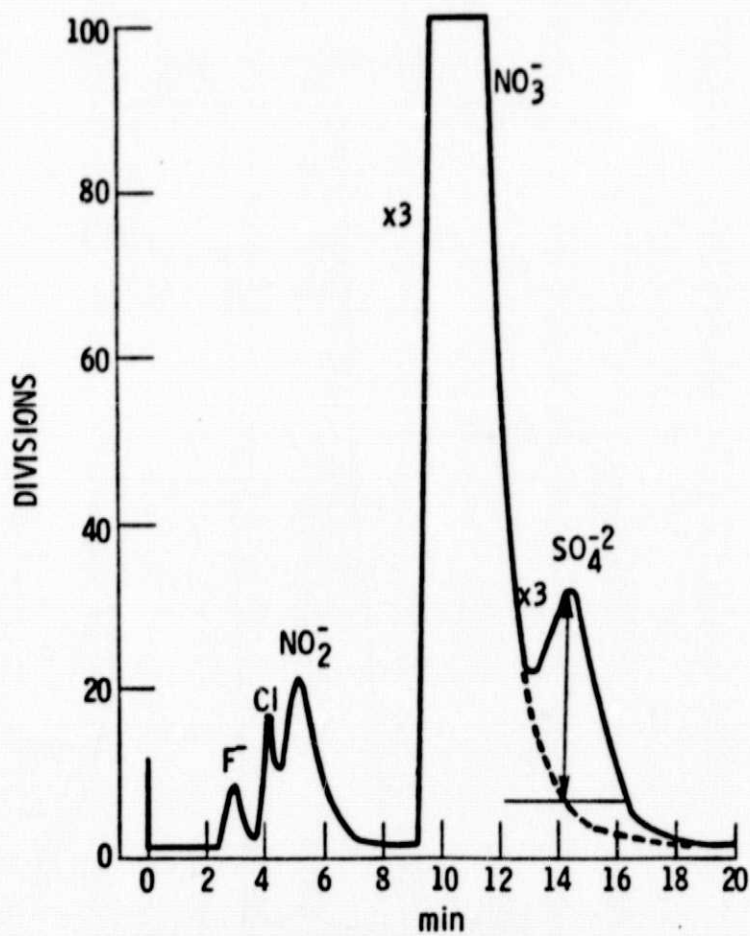


Figure 1. - Chromatogram from 0.8376 g Jet-A fuel. Dotted line indicates baseline correction made with an overlay.

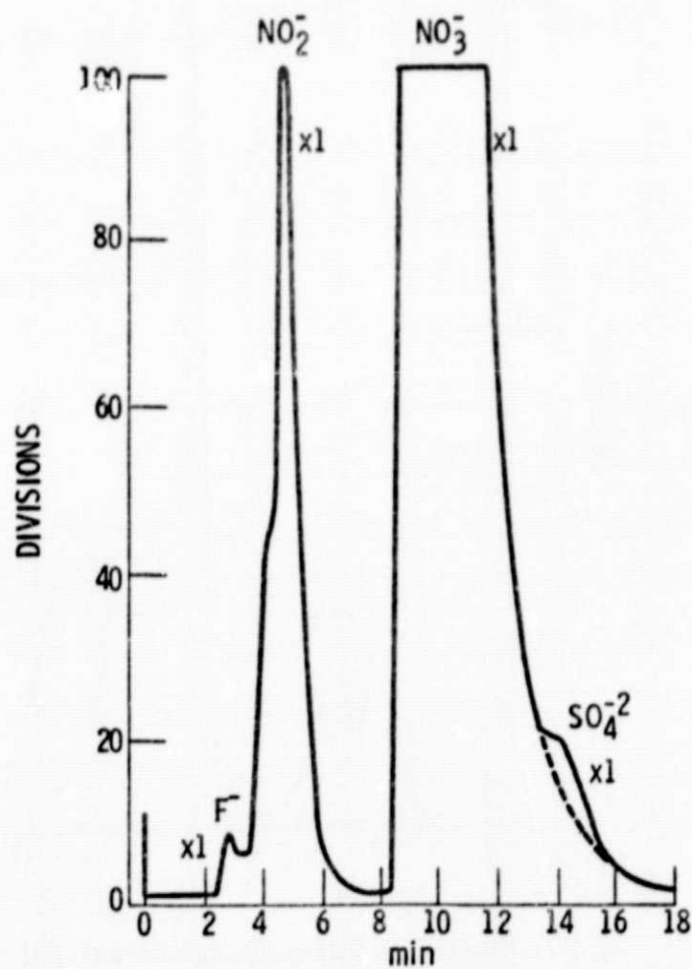


Figure 2. - Chromatogram from 0.8343 g of no. 33366 Tosco fuel showing the sulfate peak as a shoulder of the nitrate peak. The sulfate content was calculated to be 0.22 ppm.

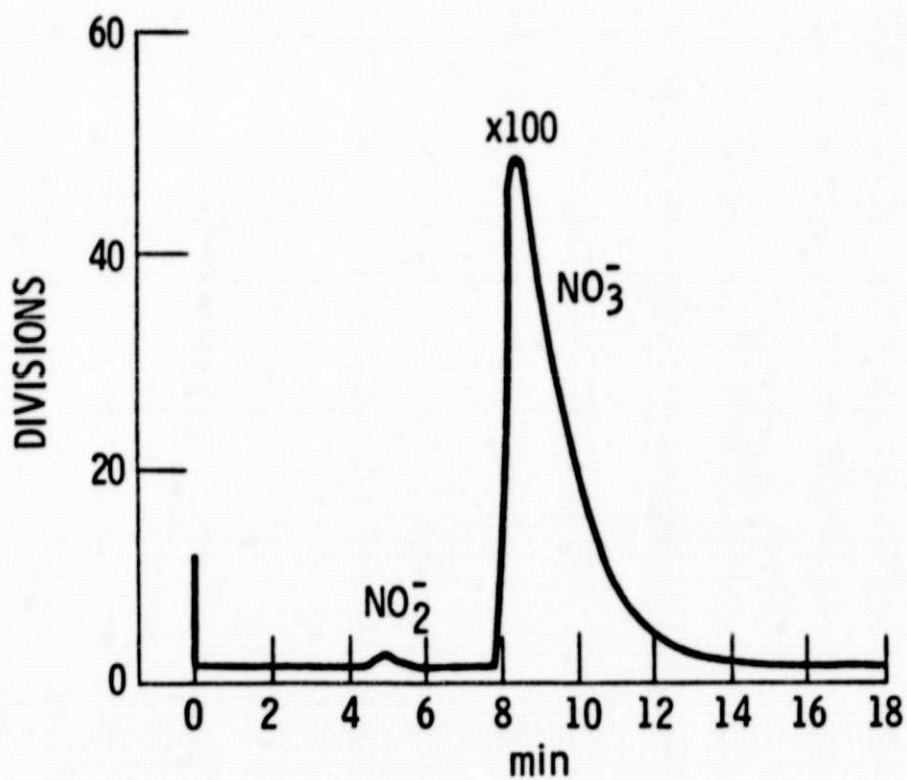


Figure 3. - Chromatogram from 0.9423 g benzoic acid oxidized without the purging step. Nitrate peak elutes on an attenuation setting of 100 μmho .

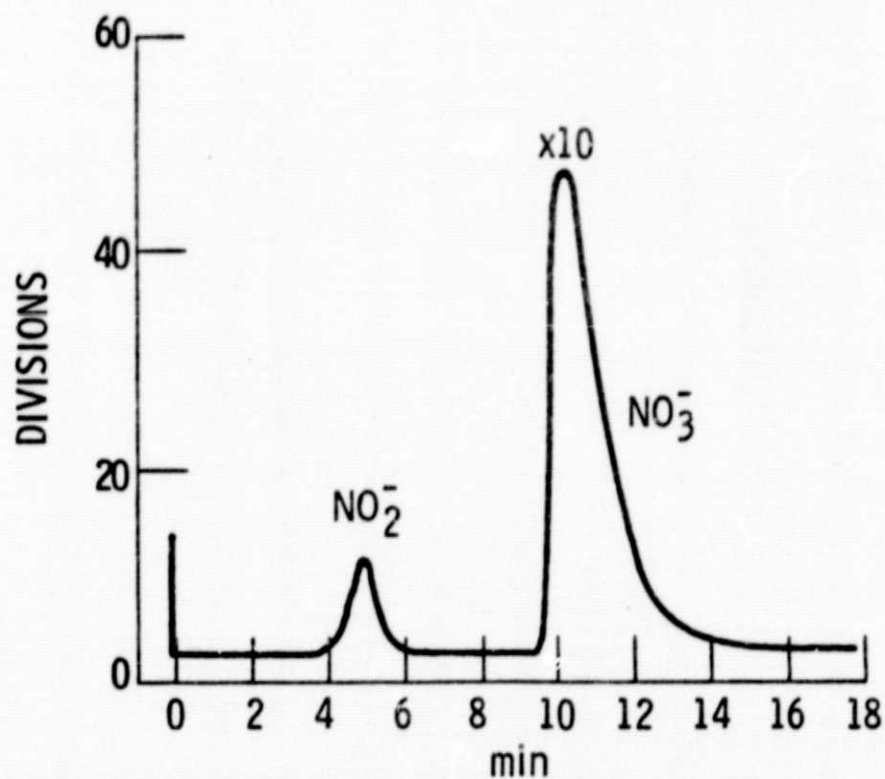


Figure 4. - Chromatogram from 1.0036 g benzoic acid oxidized with four purgings. Nitrate peak has been reduced by a factor of 10.

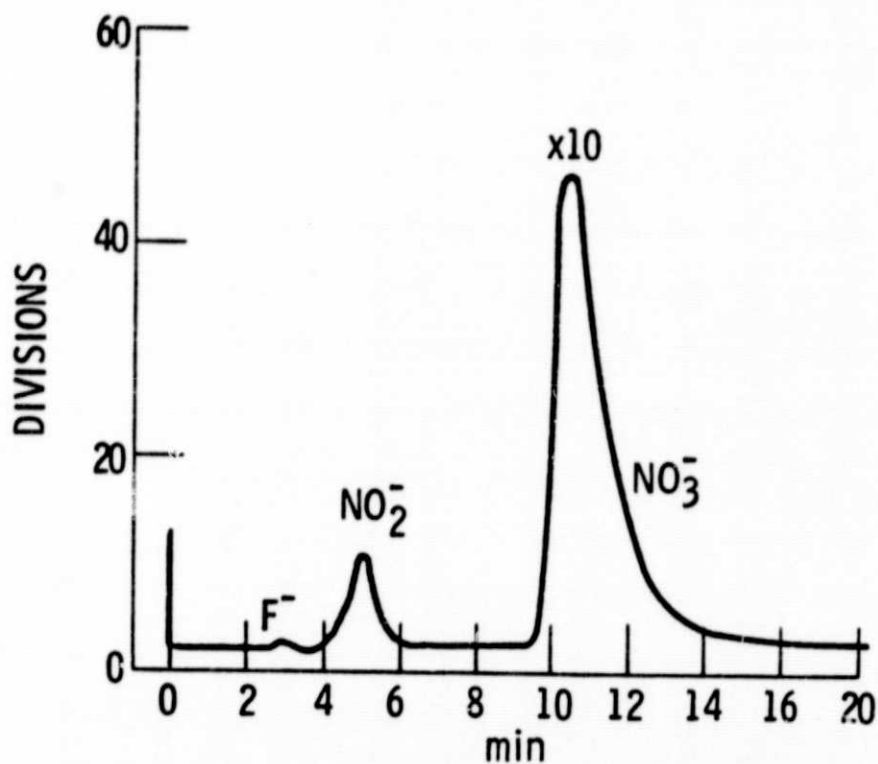


Figure 5. - Chromatogram from 0.9947 g benzoic acid oxidized with eight purgings nitrate peak has not been significantly reduced from that in figure 4.

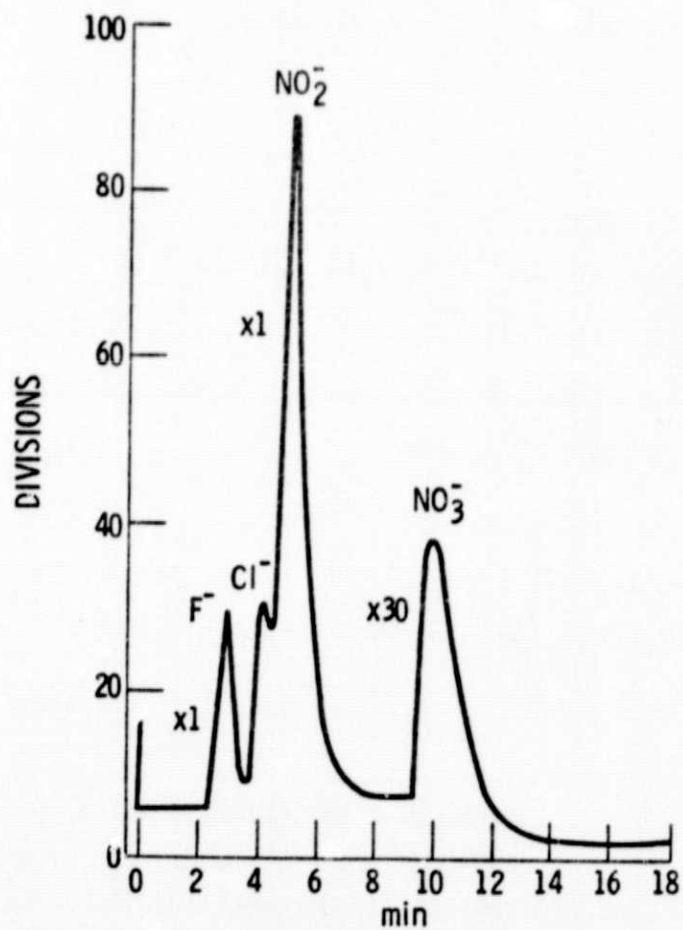


Figure 6. - Chromatogram from 0.8306 g
Tosco no. 33368 fuel showing no
sulfate peak but rather a nitrite peak.

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